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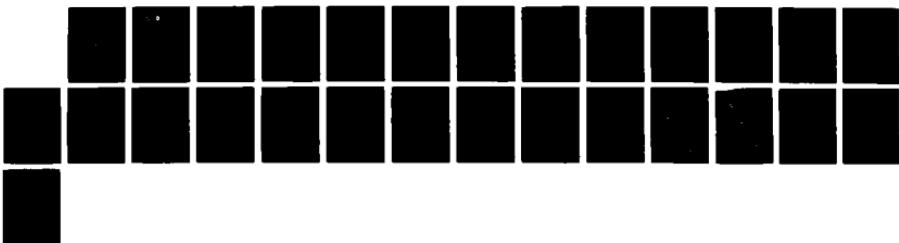
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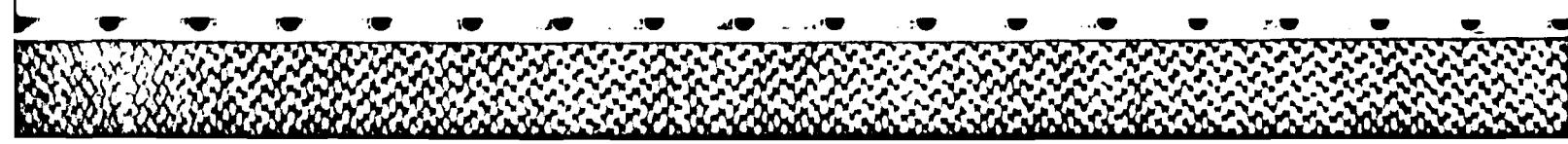
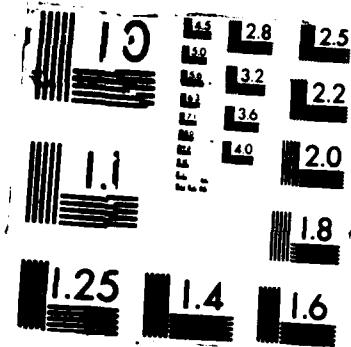
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TECHNICAL REPORT NO. 2

REACTIONS OF BH₃ WITH CO, NO, O₂, C₂H₄,
AND H₂O USING DIODE LASER ABSORPTION

by

L. PASTERNACK, R. JEFFREY BALLA AND H.H. NELSON

Prepared for publication

in the

Journal of Physical Chemistry

CHEMISTRY DIVISION
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JULY 1987

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Submitted to J. Phys. Chem.

REACTIONS OF BH₃ WITH CO, NO, O₂, C₂H₄, AND H₂O USING DIODE
LASER ABSORPTION

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Abstract

Absolute rate constants for the reaction of BH_3 with CO, NO, C_2H_4 and upper limits for the reaction of BH_3 with O_2 and H_2O are reported using a diode laser to probe BH_3 disappearance. The reactions were studied at room temperature over a pressure range of 6 to 620 torr using N_2 as a buffer gas. The rate constant for reaction of $\text{BH}_3 + \text{CO}$ was found to be in the intermediate pressure regime over the pressure range 10 to 620 torr of N_2 with rate constants ranging from $1.5 \times 10^{-13} \text{ cm}^3\text{s}^{-1}$. For $\text{BH}_3 + \text{NO}$, the rate constant was found to approach the high pressure limit of $3.7 \times 10^{-13} \text{ cm}^3\text{s}^{-1}$ at pressures above ≈ 200 torr of N_2 . The pressure independent rate constant ($p \geq 6$ torr) for the reaction of $\text{BH}_3 + \text{C}_2\text{H}_4$ was found to be $5.2 \times 10^{-11} \text{ cm}^3\text{s}^{-1}$. The reactions of $\text{BH}_3 + \text{O}_2$ and $\text{BH}_3 + \text{H}_2\text{O}$ were slower than could be measured in these experiments. Upper limits of $5 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$ and $6 \times 10^{-15} \text{ cm}^3\text{s}^{-1}$ respectively were placed on the rates of these reactions.

Introduction

There has been a resurgence of interest in the reactions of boranes due to the need to develop boron-assisted propellants. In studying the combustion of these systems, it has become evident that there is a lack of knowledge about basic chemical processes involving small boron containing species.¹⁻³ Although several models for B/O/H and B/C/O/H combustion have been proposed^{2,4} there are still large uncertainties in the thermochemistry of key radicals in the models and very few rate constants have been measured.

In this paper we report rate constants from the measurement of BH_3 reactions with CO, NO, and C_2H_4 and upper limits for the rate constants for BH_3 reactions with O_2 and H_2O . There are no previous experimental measurements of the rates of these reactions, with the exception of $\text{BH}_3 + \text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{BC}_2\text{H}_5$ which has been reported by Fehlner.⁵ Several other elementary reactions of BH_3 have previously been studied in order to determine initial products and measure rate constants.⁶ It has been found that, in general, BH_3 reactions proceed via adduct formation followed by rearrangement or elimination.³

We use a tunable diode laser as the probe source in a pump-probe experiment to study the kinetics of BH_3 . The technique has been described previously.⁷ BH_3 is formed by excimer laser photolysis (193 nm) of B_2H_6 as described by Irion and Kompa⁸ and detected by IR absorption using a tunable diode laser at the frequency of a rotation line of the ν_2 vibration of BH_3 .⁹ We measure the rate of disappearance of BH_3 with added reactant gases.

Experimental

The reaction cell is a cylindrical pyrex tube of 2m length and 4cm diameter with BaF₂ windows. The BH₃ radicals are produced by 193 nm photolysis of diborane using an ArF excimer laser (Lumonics, Model 860). The excimer beam is mildly focussed by a 2m focal length lens and turned 90° by a dichroic beam splitter (Acton Research). The radical concentration is probed using a tunable diode laser (Laser Analytics, Model LS-3) operating near 1140 cm⁻¹. The IR radiation is transmitted by the dichroic beam splitter and makes 3 passes through the reaction cell. This arrangement permits collinear propagation of the pump and probe lasers. After passing through the reaction cell, the IR radiation from the diode laser passes through a 0.5m monochromator which selects a single laser emission mode. The probe laser intensity is measured using a HgCdTe detector. A schematic of the apparatus is shown in Figure 1.

The tunable diode laser is a cryogenically cooled lead-salt diode that emits cw radiation in many monochromatic and near monochromatic modes. Tuning is accomplished by varying either the refrigerator temperature or the laser current. A reference cell or a one inch germanium etalon is placed in the beam for wavelength calibration. After the wavelength for IR absorption by the radical has been determined, the temperature and current to the diode are fixed and the monochromator is set to pass the wavelength of the absorption.

To collect kinetic data, the diode laser frequency is tuned to the absorption feature of interest. The digital oscilloscope (LeCroy model 9400) and excimer laser are triggered sequentially to obtain the transient absorption signal. The oscilloscope is used to digitize and average the signal from 50-500 experimental repetitions. The signal is then sent to an IBM PC-AT for processing. A typical plot of the transient absorption of BH₃ is shown in Figure 2 using the ν₂, J=6 line at 1141.0245 cm⁻¹.⁹ The intensity of the

absorption feature is less than 2% of the diode laser intensity to maintain linearity of signal with concentration.

The positions of some of the rotational lines in the Q branch of the ν_2 vibrational band of $^{11}\text{BH}_3$ ($X^1\text{A}'_1$) have been determined by Kawaguchi et al.⁹ They have identified the positions of lines with $J=1$ to 9 of the ${}^q\text{Q}(J,K=J)$ branch in the region from 1140.5 to 1142.8 cm^{-1} . In this region, we use NH_3 and N_2O as reference gases.¹⁰ Although there is overlap from the very strong ν_{18} band of B_2H_6 at 1172 cm^{-1} ,¹¹ we are able to discriminate between the B_2H_6 and BH_3 lines because of the high resolution of the diode laser. We have also produced BH_3 from BH_3CO photolysis at 193 nm and there is less interference from BH_3CO than from B_2H_6 in this wavelength region. However, we observed a lower quantum yield for BH_3 production from BH_3CO than from B_2H_6 . In addition, BH_3CO must be synthesized (following the method of Burg and Schlesinger¹²). Since our experiments required a relatively fast flow of materials to reduce product buildup, we primarily photolyzed B_2H_6 rather than BH_3CO .

Experiments are performed under pseudo-first-order conditions with the reactant gas present in large excess over BH_3 . When no reactant gas is added, we observe a slow disappearance of the BH_3 absorption which we attribute to reaction with the precursor B_2H_6 and to BH_3 recombination. These rates are fast compared to diffusion and pump out rates. Under our experimental conditions with total flow rates of 2 to 20 l/min the disappearance of BH_3 with no added reactant does not depend on the residence time in the cell. Under these conditions, the BH_3 decays in the presence of reactant are first-order and can be fit by a single exponential extending over 2 to 4 reaction lifetimes. The transient absorption signal is analyzed starting 15 - 20 μs after the excimer laser pulse. This allows time for vibrational and rotational equilibration and for the diode laser frequency to stabilize after the rf pulse generated by the firing of the excimer laser.

The pressure of the precursor B_2H_6 was typically 80 - 90 mtorr. At these pressures, less than 10% of the excimer laser photons were absorbed by the precursor over the 2m path thus generating a homogeneous concentration of BH_3 over the length of the cell. For the $BH_3 + C_2H_4$ reaction studies the pressure of the precursor was reduced to 10 to 20 mtorr to enable the reactant gas to be present in large excess over BH_3 to maintain pseudo-first-order conditions.

Metered flows of the precursor (B_2H_6), reactants (C_2H_4 , CO, NO, O_2 , and H_2O) and buffer gases (N_2 and SF_6) were mixed and flowed through the cell using Tylan mass flow controllers and mass flow meters. The following gases were used without further purification: B_2H_6 (Matheson, 1% in He and 30% in He), N_2 and O_2 (Air Products, Industrial Grade purity), and SF_6 , C_2H_4 , CO, and NO (Matheson, Commercial purity). Water was admitted to the cell both by using a bubbler with N_2 and by using premixed tanks of water saturated N_2 .

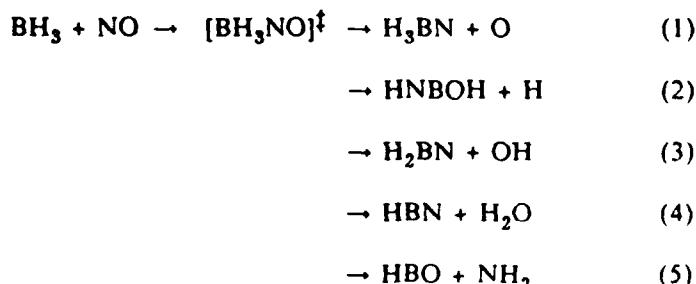
Results and Discussion

$\text{BH}_3 + \text{CO}$ reactions. The reaction of $\text{BH}_3 + \text{CO} \rightarrow \text{BH}_3\text{CO}$ is expected to be exothermic by approximately 23 kcal/mole.¹ We measured the rate of reaction of BH_3 with CO at total pressures of 10 to 600 torr at room temperature. A typical time resolved plot of the transient absorption of BH_3 in the presence of CO is shown in Figure 2. The curve shown is the result of averaging 100 experimental repetitions. The first-order decay constant is obtained from the slope of the log of the absorption signal vs. time, using a weighted linear-least-squares fitting technique. Second-order rate constants at a given total pressure are obtained from a plot of first-order rate constants vs. reactant pressure, as shown in Figure 3. The intercept represents the sum of all BH_3 removal processes other than reaction with CO. These are typically at least an order of magnitude slower than the fastest measured first-order decay constant. The pressure dependence of this reaction was measured using N_2 as a buffer gas at total pressures of 10 to 600 torr. The results are shown in Figure 4 and listed in Table I. The uncertainties listed in Table I ($\pm 2\sigma$) refer to the precision of the data as determined from the scatter in the second-order plots. In general, the high pressure data is the least precise, due to pressure broadening of the absorption. We also used SF_6 as a buffer gas and found it to be about a factor of 2 more efficient at promoting this reaction. However, SF_6 weakly absorbs 1140 cm^{-1} radiation and therefore could not be used as a buffer gas at high pressures. From Figure 4, it is evident that the high pressure limit for the $\text{BH}_3 + \text{CO}$ reaction is likely greater than $10^{-11} \text{ cm}^3\text{s}^{-1}$ and is approached at greater than atmospheric pressure.

There are no prior direct measurements of the $\text{BH}_3 + \text{CO} + \text{M} \rightarrow \text{BH}_3\text{CO} + \text{M}$ reaction. By comparison to the $\text{BH}_3 + \text{PF}_3$ reaction measured by Fridmann and Fehlner,¹³ Bauer¹ concludes that the rate should be approximately $3 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$. However, these experiments were performed at 500K and 6 torr total pressure in helium.

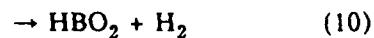
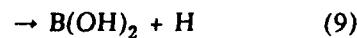
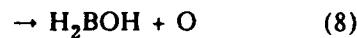
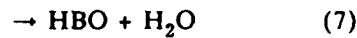
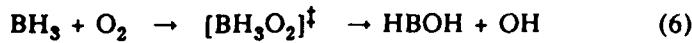
BH₃ + NO reactions. We have measured the reaction of BH₃ with NO at room temperature at total pressures of 11 to 310 torr using N₂ as a buffer gas. Experiments were performed analogously to the BH₃ + CO experiments. The second-order rate constants are listed in Table 2 and shown as a function of total reaction pressure in Figure 5. We approach a high pressure limit to the rate constant for the BH₃ + NO reaction of approximately $3.7 \times 10^{-13} \text{ cm}^3\text{s}^{-1}$. The pressure at which the high pressure limit is reached is on the order of 200 torr of N₂. This is in contrast to the BH₃ + CO reaction where the high pressure limit to the rate constant was found to occur at pressures greater than atmospheric.

There have been no previous measurements of the BH₃ + NO reaction. Hoffmann and Engelhardt¹⁴ have observed a low concentration of the BH₃NO complex from BH₃CO + NO reactions using mass spectroscopy. The different pressure dependence of the BH₃ + CO and BH₃ + NO reactions suggest that a mechanism other than complex stabilization might be involved. The thermochemistry of species containing boron and nitrogen is not well known so it is difficult to determine whether products from rearrangement or elimination channels are exothermic. Some possible exothermic channels, all of which involve extensive rearrangement, include:



$BH_3 + O_2$ reactions. The reaction of $BH_3 + O_2$ has several exothermic pathways, all of which involve extensive rearrangement, similar to the $BH_3 + NO$ reaction pathways.

These include:



Unlike $BH_3 + NO$, we see no apparent disappearance of BH_3 with pressures of 100 torr of O_2 at total pressures up to 400 torr with N_2 buffer gas. It is possible that spin constraints lead to large barriers in some of the $BH_3 + O_2$ channels which would not occur in $BH_3 + NO$ reactions.

The BH_3 signal does not decay exponentially in the presence of large amounts of O_2 . This is most likely due to the formation of a significant amount of O^3P atoms from 193 nm photolysis of O_2 . The O^3P may react with B_2H_6 to generate BH_3 from the reaction $O^3P + B_2H_6 \rightarrow BH_3O + BH_3$. This reaction has been proposed as a step in diborane oxidation.¹⁵ From our results, we estimate that the rate of reaction of $BH_3 + O_2$ is less than $5 \times 10^{-15} \text{ cm}^3 \text{s}^{-1}$. Although there are no prior measurements of this reaction, Shaub and Lin⁴ estimate the rate constant for reaction (6) to be $7 \times 10^{-17} \text{ cm}^3 \text{s}^{-1}$ from their model of diborane oxidation.

$BH_3 + C_2H_4$ reactions. We have measured the rate of reaction of $BH_3 + C_2H_4$ to be $(5.2 \pm 1.0) \times 10^{-11} \text{ cm}^3\text{s}^{-1}$ at room temperature. By monitoring the rate of disappearance of BH_3 in the presence of excess C_2H_4 at a series of ethylene pressures we determined second-order rate constants for this reaction using the same techniques as in the other BH_3 reactions presented in this report. The experiments were performed at 9 different total pressures between 6 and 90 torr using N_2 as a buffer gas. We observed no pressure dependence for this reaction. Our results are reported in Table 3.

The hydroboration reaction has been studied more extensively than the other reactions reported in this paper. Fehlner⁵ has measured the rate of production of ethylborane ($C_2H_5BH_2$) from this reaction at temperatures from 430 to 590K and 4.7 torr total pressure in helium to be in the range of $1.5 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ to $4.2 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$, which is more than an order of magnitude slower than our room temperature results. If we assume that this represents the high pressure limit for the reaction and that the only pathway is to ethylborane formation, we can combine their results with ours to determine an activation energy of -4 kcal/mole for this reaction.

There have also been several theoretical studies of this reaction.¹⁶⁻¹⁹ The reaction to form ethylborane is predicted to proceed through a two step mechanism.^{17,19} The first step involves the formation of a π -complex held together by a three center CBC bond. The complex is calculated to be 10 kcal/mole more stable than the reactants.¹⁷ The second step involves the formation of a transition state via a donation-back-donation mechanism. In this step a transition state is postulated in which ethylene donates electrons through a carbon atom to the vacant orbital on boron at the same time as a hydrogen on BH_3 donates electrons back to the other carbon atom of ethylene in a four center arrangement. The calculations of Sundberg et al.¹⁷ show no activation barrier for this reaction. Nagase et al.¹⁹ predict an activation energy of ~4 kcal/mole.

BH₃ + H₂O reactions. We observe no reaction between BH₃ and H₂O with 5 torr of water and total pressures up to 200 torr using N₂ as a buffer gas. Water was introduced into the reaction cell both by bubbling N₂ through water and by making mixtures of H₂O in N₂. We were able to confirm the presence and concentration of water in the cell by monitoring absorption in the ν₂ band of H₂O in the region 1120 - 1142 cm⁻¹.^{20,21} In addition, by monitoring the B₂H₆ absorption both with and without added water, we did not observe room temperature reaction between B₂H₆ and H₂O, although Weiss and Shapiro²² have observed diborane hydrolysis at 324K. We estimate that the rate constant for reaction of BH₃ + H₂O is less than 6×10^{-15} cm³s⁻¹.

Shaub and Lin⁴ predict a room temperature rate constant of 7×10^{-17} cm³s⁻¹ for the BH₃+H₂O reaction from their model of diborane oxidation. However, Weiss and Shapiro²² have postulated that one step in the hydrolysis of diborane at 324K is BH₃ + H₂O → [H₃BH₂O][‡] → BH₂OH + H₂. Based on the work of Weiss and Shapiro, Bauer has derived a rate constant for the BH₃ + H₂O reaction of approximately 10⁻¹³ cm³ s⁻¹. The disagreement between our results for the BH₃ + H₂O reaction and the results derived from the experiments of Weiss and Shapiro may be indicative of a different mechanism for the diborane hydrolysis than that which they proposed. However, evidence for the existence of a borane-water complex comes from a kinetic study of the intermediates in hydroborate ion hydrolysis by Wang and Jolly.²³ In addition, Dill et al.²⁴ have calculated a configuration for this complex that is stable relative to BH₃ + H₂O by 6 kcal/mole. In this complex, BH₃ and H₂O are in a staggered conformation.

Conclusions

We have studied the reactions of BH_3 with CO, O_2 , NO, H_2O and C_2H_4 . It is difficult to justify our results in terms of the model for BH_3 reactions proposed by Fehlner.³ By this theory, BH_3 reactions are expected to proceed via reaction with Lewis bases to produce tetra-coordinate boron compounds. These reactions are expected to be fast. Consequently they involve early transition states which result from reactions controlled by early interactions. For BH_3 reactions, these interactions are due to the attractive force generated by the empty B $2p_z$ orbital and the donor p_σ orbital.³ Although this type of reaction is expected to be faster for reactants containing lower nuclear charge, it is difficult to justify such large differences in rates and pressure dependences as we observe. Our results suggest that different mechanisms may be involved for BH_3 reactions with CO, O_2 , and NO. Theoretical calculations on BH_3CO , BH_3NO , and BH_3O_2 complexes could help determine the mechanism. Experimental studies to determine reaction products would also be useful.

Acknowledgment

We thank Dr. J. E. Butler for providing the BH_3 spectroscopic information prior to publication. We also thank Dr. S. H. Bauer for providing reference 1 prior to publication and for his helpful discussions.

Table 1. Room temperature rate constants for the reaction of $\text{BH}_3 + \text{CO}$ with N_2 buffer gas ($\pm 2\sigma$).

Total Pressure (torr)	$k \times 10^{13}$ (cm^3s^{-1})
10	1.5 ± 0.1
10	1.7 ± 0.1
20	2.7 ± 0.4
30	4.3 ± 0.7
40	4.6 ± 0.6
50	5.4 ± 1.0
60	6.6 ± 0.8
80	6.2 ± 0.8
100	9.9 ± 2.3
100	12.0 ± 2.3
203	16.6 ± 2.1
300	21.0 ± 3.1
400	21.7 ± 4.1
400	22.6 ± 3.4
500	39.6 ± 5.7
500	34.6 ± 4.6
600	38.8 ± 5.6
620	46.6 ± 4.3

Table 2. Room temperature rate constants for the reaction of
 $\text{BH}_3 + \text{NO}$ with N_2 buffer gas ($\pm 2\sigma$).

Total Pressure (torr)	$k \times 10^{13}$ (cm^3s^{-1})
11	2.0 ± 0.2
52	2.9 ± 0.3
100	3.0 ± 0.6
200	3.7 ± 1.3
310	3.7 ± 0.6

Table 3. Room temperature rate constants for the reaction of
 $\text{BH}_3 + \text{C}_2\text{H}_4$ with N_2 buffer gas ($\pm 2\sigma$).

Total Pressure (torr)	$k \times 10^{11}$ (cm^3s^{-1})
6	5.2 ± 1.8
12	5.7 ± 1.7
20	5.1 ± 0.4
22	5.4 ± 0.8
45	4.3 ± 0.8
46	4.1 ± 0.6
47	3.5 ± 0.4
88	7.1 ± 2.7
89	6.0 ± 2.1

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Figures

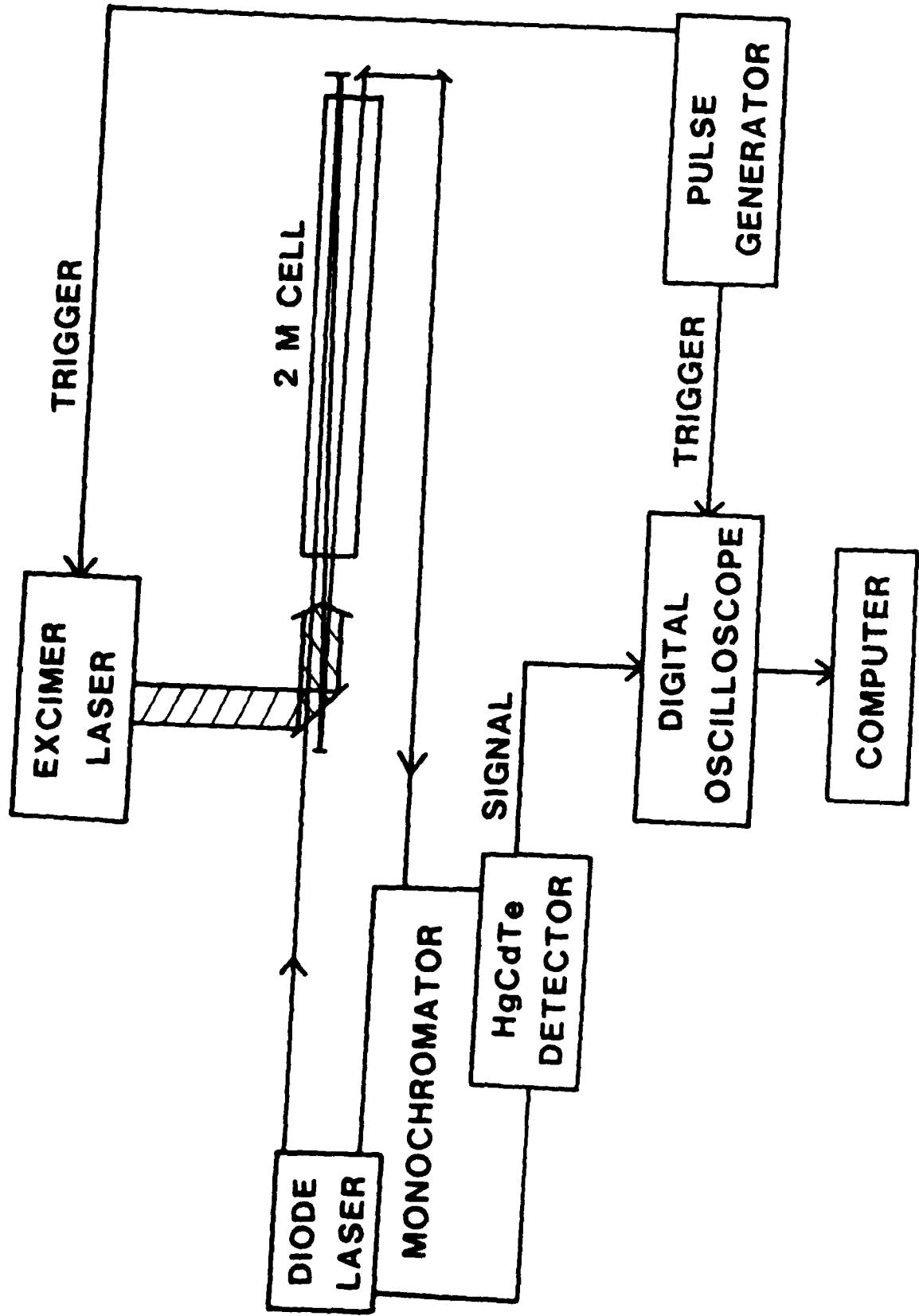
Fig. 1. Schematic diagram of the apparatus.

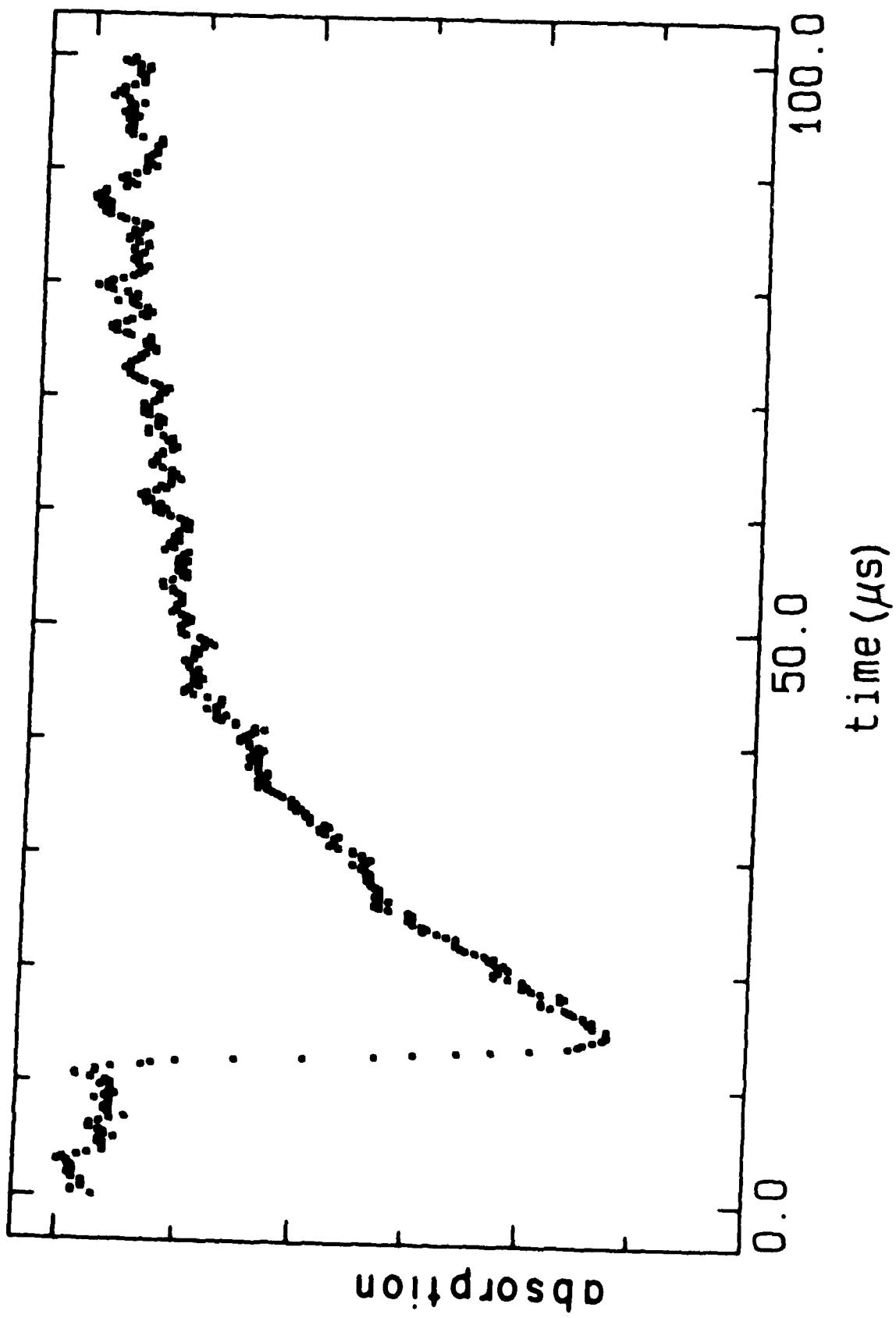
Fig. 2. Plot of the transient absorption (in arbitrary units) of BH_3 for the reaction of $\text{BH}_3 + \text{CO}$. The plot is from the average of 100 decays at 298K. $P(\text{B}_2\text{H}_6)=66$ mtorr, $P(\text{CO})=3$ torr, and $P(\text{total})=50$ torr using N_2 is a buffer gas. The oscilloscope is triggered 10 μs prior to the excimer laser.

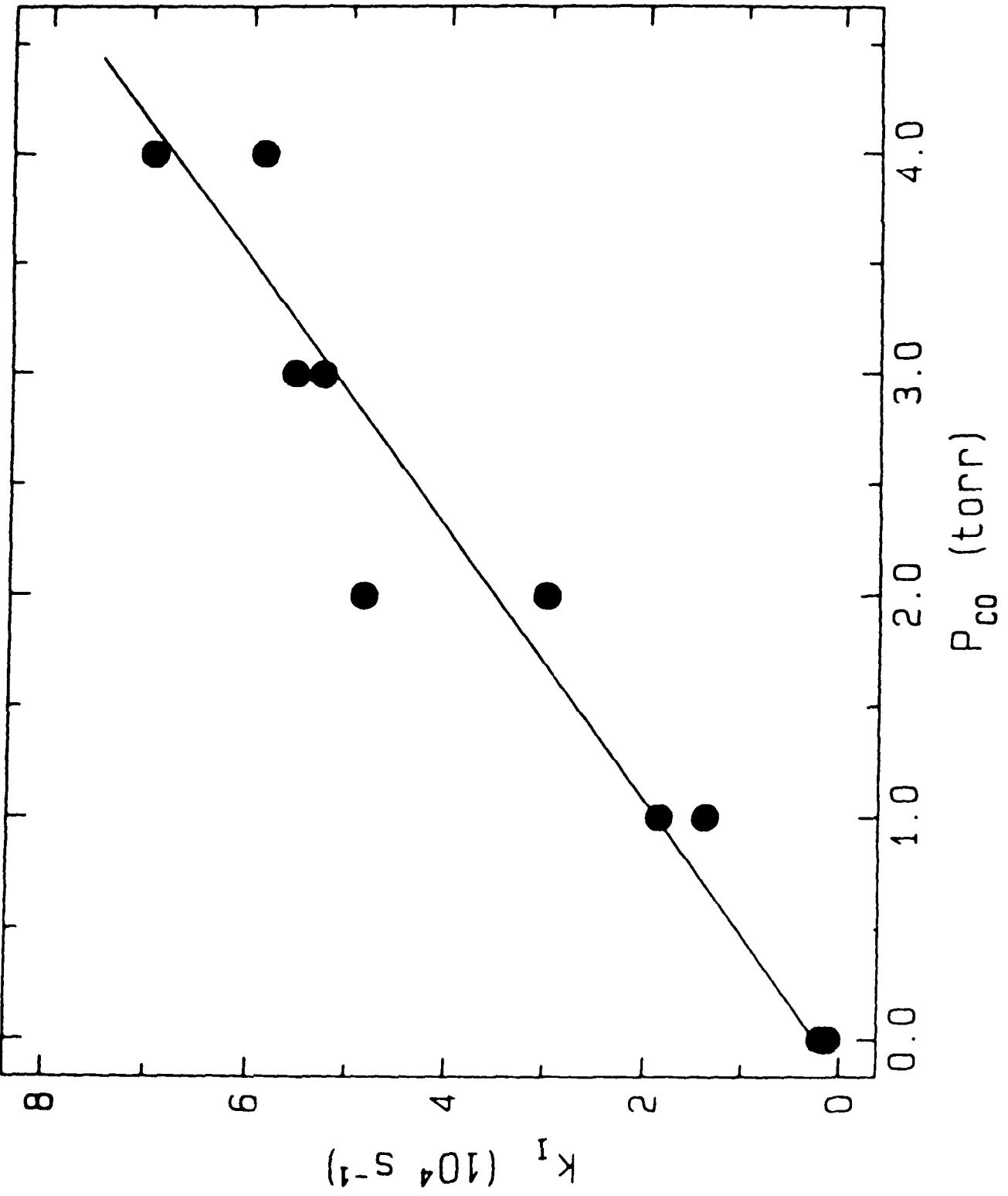
Fig. 3. Plot of the observed BH_3 decay constant, k_1 , vs CO pressure for the reaction of $\text{BH}_3 + \text{CO}$ at 298K. N_2 was used as a buffer gas. $P(\text{B}_2\text{H}_6) = 66$ mtorr and the total pressure was 50 torr. The slope gives a reaction rate of $5.4 \times 10^{-12} \text{ cm}^3\text{s}^{-1}$ and the intercept represents the rate for other BH_3 removal processes.

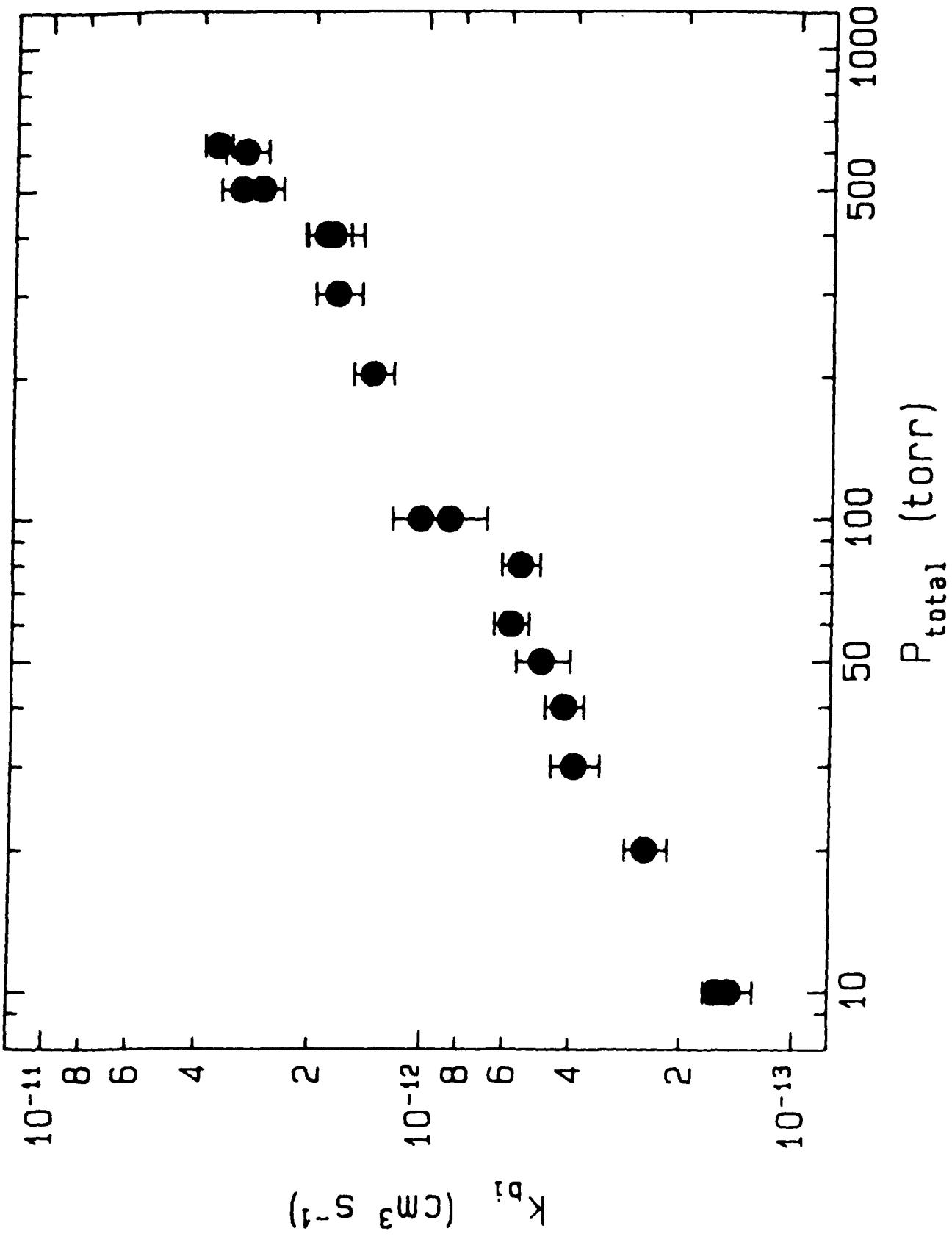
Fig. 4. Pressure dependence of the bimolecular rate constant for the reaction of BH_3 with CO at 298K. The buffer gas used is N_2 . The error bars represent $\pm 2\sigma$.

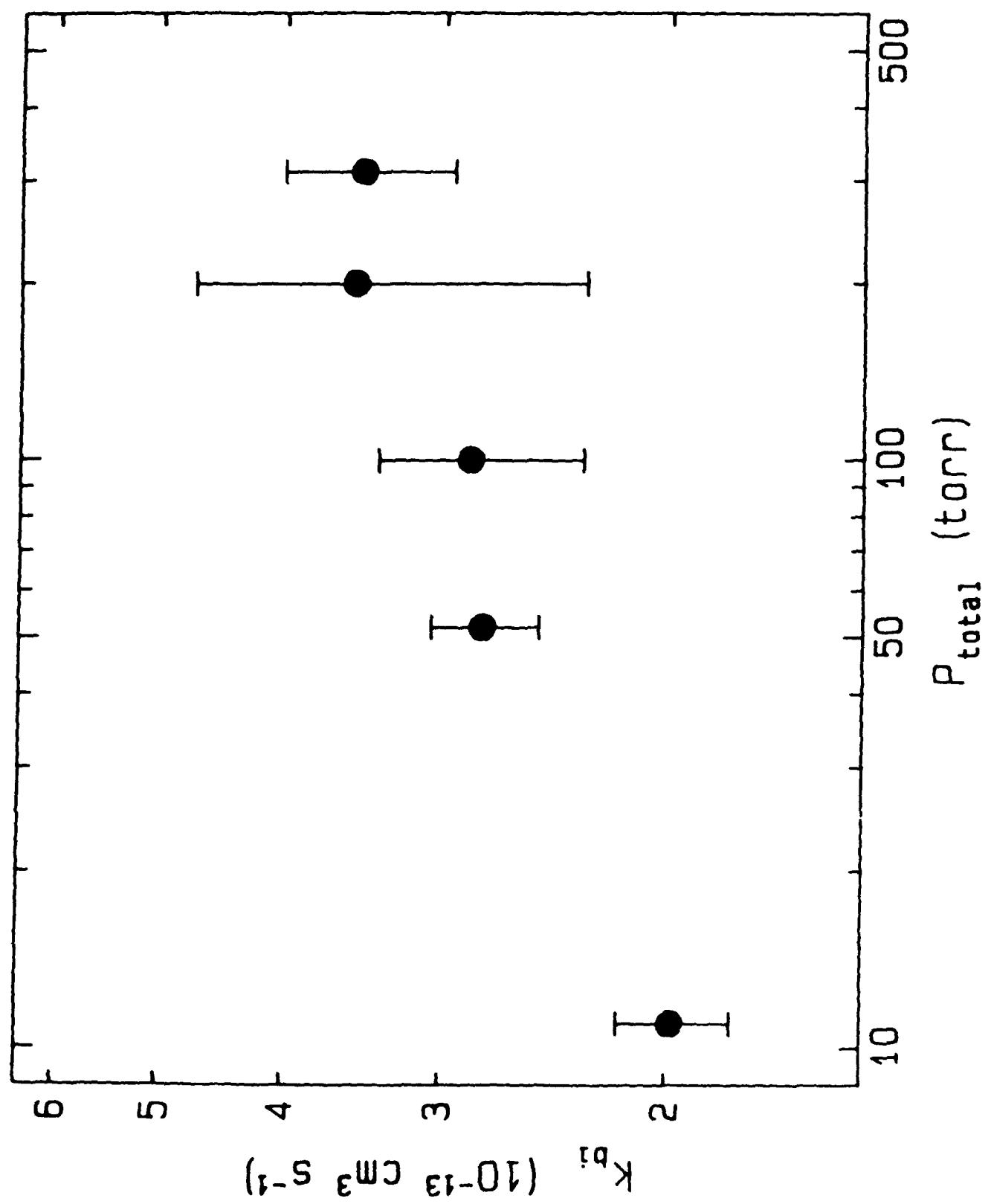
Fig. 5. Pressure dependence of the bimolecular rate constant for the reaction of BH_3 with NO at 298K. The buffer gas used is N_2 . The error bars represent $\pm 2\sigma$











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